

**PATENT APPLICATION**  
**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of

Docket No: Q93199

Eiji HONDA, et al.

Appln. No.: 10/571,317

Group Art Unit: 1796

Confirmation No.: 8365

Examiner: Robert C. BOYLE

Filed: March 9, 2006

For: STABILIZED FLUOROPOLYMER AND METHOD FOR PRODUCING SAME

**DECLARATION UNDER 37 C.F.R. § 1.132**

Mail Stop Amendment  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Tadashi Ino, hereby declare and state:

THAT I received a Masters degree in Science from the Department of Molecular Engineering in March of 1986 from Kyoto University, Graduate School of Engineering;

THAT I have been employed by DAIKIN INDUSTRIES, LTD. since 1986, where I hold a position as a researcher, with responsibility for development of a fluoropolymer used in fuel cell;

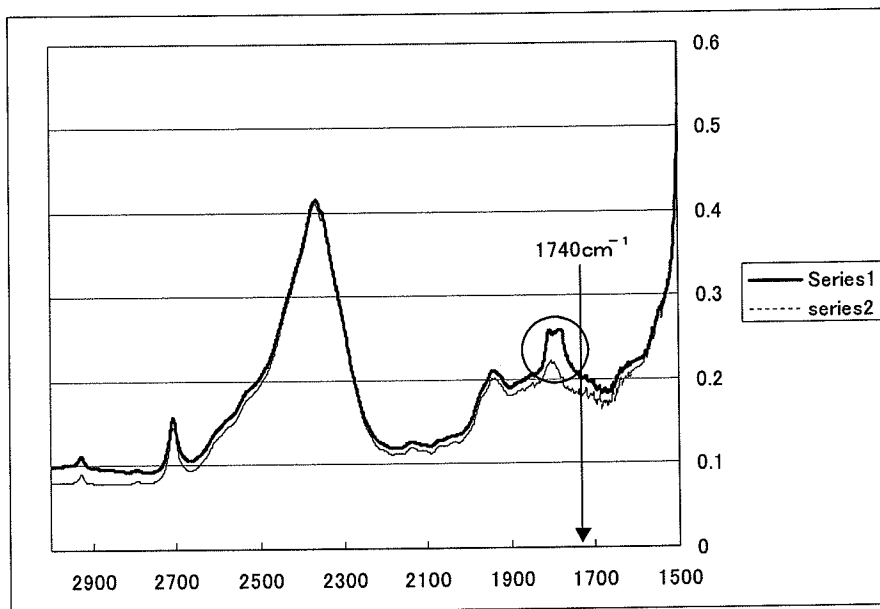
THAT I am a co-inventor of the invention described and claimed in the above-identified application; and

THAT I am familiar with the Office Action dated June 29, 2009 and the Advisory Action dated October 6, 2009, where the pending claims stand rejected over one or more of U.S. Patent 6,150,426 to Curtin et al, U.S. Patent 3,085,083 to Schreyer and WO 02/096983 to Hasegawa et al.

I offer my opinion below as to the state of the art and what one of ordinary skill would understand from the references cited by the Examiner. Further, the following experiment was carried out, either by me or under my direct supervision.

### **EXPERIMENT**

Graph 1 below shows the IR profiles of the fluoropolymers prepared in Example 1 of my specification. Fluoropolymer A (prior to fluorination) had an intensity ratio [x/y] between the carboxyl group-due peak [x] and the  $\text{-CF}_2\text{-}$  group-due peak [y] of 0.23. Stabilized Fluoropolymer B, following fluorination, had an intensity ratio [x/y] of 0.03 (page 37, lines 22-25 and page 48, lines 19-22 of the specification). The IR profiles of fluoropolymers A and B are overlaid in Graph 1 below. The solid line is IR profile of Fluoropolymer A, whereas the dotted line shows the IR profile of stabilized Fluoropolymer B. The carboxyl group-due peak is circled.



Solid line: Fluoropolymer A

Dotted line: Stabilized Fluoropolymer B

Circled area: carboxyl group-due peak

### **DISCUSSION**

(1) Claims 9 and 12-14 stand rejected under 35 U.S.C. § 102(b) as anticipated by or, in the alternative, under 35 U.S.C. § 103(a) as obvious over U.S. Patent 6,150,426 to Curtin et al.

Because Curtin et al is said to teach copolymers of TFE and a perfluorinated vinyl ether “preferably substantially free of components containing carbonyl bonds,” the Examiner considered that the intensity ratio  $[x/y]$  of not higher than 0.05 in IR measurement is met by Curtin et al. In the Advisory Action dated October 6, 2009, the Examiner maintained that “free of components containing carbonyl bonds” means the absence of all functional groups containing a carbon-oxygen double bond, including carboxyl group. The Examiner further noted that Curtin et al contrast their copolymers “free of components containing carbonyl groups” from those of U.S. Patent 4,433,082 to Grot indicating bands at  $1740\text{ cm}^{-1}$  corresponding to the presence of carbonyl groups. Regarding this last point, the Examiner commented that “the bands at  $1740\text{ cm}^{-1}$  do not apply to the invention of Curtin, but rather show the difference between Curtin and the prior art.”

Claim 9 is directed to a stabilized fluoropolymer represented by formula (II), which stabilized fluoropolymer shows an intensity ratio  $[x/y]$  between carboxyl group-due peak  $[x]$  and  $-\text{CF}_2-$  due peak  $[y]$  no higher than 0.05 in IR measurement.

Curtin et al relates to a process for preparing a composition comprising particles of highly fluorinated ion-exchange polymer having sulfonate functional groups, which process comprises contacting the polymer in a pressurized vessel with an aqueous liquid dispersion medium under conditions which cause the polymer to form particles, cooling the contents of the vessel, and recovering the desired product.

1. The polymer of Curtin et al necessarily has a carboxyl end group

Curtin et al identifies the polymers disclosed in U.S. Patent 3,282,875 to Connolly et al as being preferred polymers for use in their invention. See col. 4, lines 30-32 of Curtin et al. Although U.S. Patent 3,282,875 and Curtin et al do not disclose an end group of a polymer, GB 1,210,794 discloses that the polymer of U.S. Patent 3,282,875 has an unstable carboxyl group. See Examples 1, 6 and 9 in Table I of GB '794 employing the copolymer of Example 8 of U.S. Patent 3,282,875 (page 4, lines 96-103). As shown in Table I of GB '794, Examples 1, 6 and 9 not subjected to fluorination treatment had a carboxylate content in excess of 500 end groups/ $10^6$  C atoms.

U.S. Patent 3,085,083 to Schreyer at col. 2, lines 28-33 explains how carboxylate end-groups in a fluorocarbon polymer are formed. Particularly, carboxylate end-groups in a fluorocarbon polymer are formed when polymerization is initiated through a peroxide catalyst, or when the polymerization is terminated through the formation of a vinyl bond which is subsequently oxidized. Curtin et al does not disclose a polymerization method, but cites to U.S. Patent 3,282,875 to Connolly at col. 4, lines 31-32. Connolly et al discloses a method of producing fluorocarbon vinyl ether polymers. In polymerization, a peroxide or a redox initiator is used as an initiator, as illustrated at col. 2, lines 55-60. Namely, in the absence of subsequent treatment to remove carboxyl end groups, such carboxyl end groups are necessarily present in the copolymer of Curtin et al derived from the initiator used in polymerization.

Fluorination treatment is needed to reduce the intensity ratio [x/y]. See, for example, the unfluorinated polymer of Examples 1 and 3 of the present specification. Prior to fluorination, the polymer of Example 1 had an intensity ratio [x/y] of 0.23 (page 47, lines 23-25), and the polymer of Example 3 prior to fluorination treatment had an intensity ratio [x/y] of 0.08 (page 51, lines

26-29 of the specification). As shown above, the copolymer of Curtin et al necessarily contains carboxyl end groups derived from the initiator used in polymerization, and Curtin et al does not disclose any technique for removing carboxyl end groups. In fact, Curtin et al's investigation was unrelated to the end group of the fluoropolymer.

2. Curtin does not refer to an end group of the polymer

The passage at col. 6, lines 49-65 of Curtin et al cited by the Examiner is reproduced below.

The solid compositions, including the compositions obtained upon drying preferred liquid compositions in accordance with the invention, are preferably substantially free of components containing carbonyl bonds as determined by reflectance infrared spectroscopy. In contrast, reflectance infrared spectroscopy of solids recovered from compositions made by the process of U.S. Pat. No. 4,433,082 to Grot indicate bands at  $1740\text{ cm}^{-1}$  corresponding to the presence of carbonyl groups. It is believed that compounds containing carbonyl groups are formed during manufacturing due to the presence of alcohols in the dispersion process. Preferred compositions in accordance with the invention are also free of C-H bonds, i.e., no bands  $2800\text{-}3000\text{ cm}^{-1}$  occur in reflectance infrared spectroscopy, unless they are present in the polymer molecule, e.g., unfluorinated sites or quaternary amine cation associated with the  $\text{-SO}_3\text{-}$  group.

The band at  $1740\text{ cm}^{-1}$  corresponds to carbonyl groups in low molecular weight organic compounds. Particularly, the "carbonyl groups" are identified in the very same passage as carbonyl group-containing compounds formed during manufacturing due to the presence of alcohols in the dispersion process. That is, the "carbonyl groups" mentioned by Curtin et al are present in by-products and have nothing to do with carboxyl end groups of the copolymer.

When a carboxyl group is present at the end of a fluoropolymer, its band shifts to a larger wave number as shown in Table X below. The IR spectrum of a fluoropolymer having carboxyl

end groups does not show bands at  $1740\text{ cm}^{-1}$ . That is, the bands at  $1740\text{ cm}^{-1}$  do not include bands derived from carboxyl end groups of a fluoropolymer.

Table X

	U.S. Patent 3,085,083	U.S. Patent 4,675,380	U.S. Patent 6,689,833
-COF		$1883\text{ cm}^{-1}$	$1888\text{ cm}^{-1}$
-COOH (monomer)	$1812\text{ cm}^{-1}$	$1812\text{ cm}^{-1}$	$1813\text{ cm}^{-1}$
-COOH (dimmer)	$1779\text{ cm}^{-1}$	$1773\text{ cm}^{-1}$	$1774\text{ cm}^{-1}$
-CO <sub>2</sub> CH <sub>3</sub>		$1795\text{ cm}^{-1}$	

The shift is due to low electron density at the carbonyl carbon atom by the electron-withdrawing fluorocarbon group.

3. The reflectance infrared spectroscopy indicates very small bands

There is no disclosure in Curtin et al relating to bands corresponding to the carboxyl end groups of a fluoropolymer.

As shown in my Graph 1 above, the reflectance infrared spectroscopy indicates very small bands corresponding to the presence of carboxyl end groups of the fluoropolymer. It is easy to miss these bands and, therefore, careful observation is needed to recognize the same.

Because Curtin et al were not interested in the end group of a fluoropolymer, it is not surprising that Curtin et al do not refer to the presence of bands other than those at  $1740\text{ cm}^{-1}$ .

(2) Claims 10 and 11 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Curtin et al in view of U.S. Patent 3,085,083 to Schreyer. Curtin et al was cited as disclosing that preferred compositions are "free of C-H bonds." Schreyer was cited as teaching -CF<sub>2</sub>H end groups. The reason for rejection was that it would have been obvious that "given the

end group  $\text{-CF}_2\text{H}$  of Schreyer on a fluoropolymer that is free of C-H bonds as taught by Curtin would result in the claimed end groups of  $\text{-CF}_3$ ."

Claim 10 is directed to a stabilized fluoropolymer represented by general formula (II), wherein in a hydrolyzate of the stabilized fluoropolymer, the number [x] of main chain terminal  $\text{-CF}_3$  groups per  $1 \times 10^5$  main chain carbon atoms of the hydrolyzate is not smaller than 10 (as calculated using an integrated intensity due to main chain terminal  $\text{-CF}_3$  groups and an integrated intensity due to  $\text{-CF}_2$ - adjacent to an ether bond and side chains branched from the main chain in the hydrolyzate).

As explained above, the polymer of Curtin et al has a carboxyl end group. Further, there is no description in Curtin et al to the effect that the end group is fluorinated. Thus, the number [X] of main chain terminal  $\text{-CF}_3$  groups per  $1 \times 10^5$  main chain carbon atoms is less than 10.

The combination of Curtin et al and Schreyer also does not teach my invention. Particularly, the polymer is necessarily fluorinated to obtain a  $\text{-CF}_3$  end group.

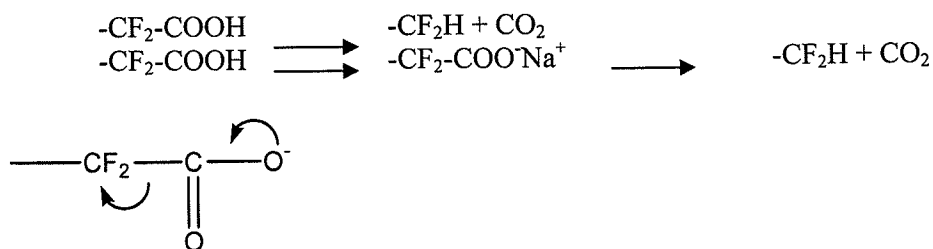
However, the end group of the polymer of Curtin et al is a carboxyl group. On the other hand, the end group of the polymer of Schreyer is a  $\text{-CF}_2\text{H}$  group such that the combination of Curtin et al results in a  $\text{-CF}_2\text{H}$  group even if Schreyer teaches that additional fluorinated methyl end groups add stability.

Moreover, neither Curtin et al nor Schreyer et al teach any stabilization method by fluorination. Thus, the combination does not provide a polymer having a  $\text{-CF}_3$  end group.

In more detail, Schreyer teaches two techniques to carry out end-capping bridging cols. 3-4, including slurry-capping and vapor-capping. Basically, in Schreyer's technique, the polymer is treated with water at elevated temperatures to form a substantial number of stable  $\text{-CF}_2\text{H}$  groups. See col. 2, lines 63-68 of Schreyer. As disclosed at col. 4, lines 10-14, the

completion of the reaction, namely, the transformation of substantially all of the carboxylate end-groups to  $-\text{CF}_2\text{H}$  end-groups, can be determined readily by infrared techniques.

Importantly, the treatment of Schreyer cannot form  $-\text{CF}_3$  end groups.



Because Curtin et al does not teach fluorination treatment, and because the treatment of Schreyer cannot form  $-\text{CF}_3$  end groups, the resulting combination can never achieve the invention of claim 10.

The statement in Curtin et al that the fluoropolymer is then “free of C-H bonds” refers to a (per)fluoropolymer having  $-\text{CF}_2-$  but no  $-\text{CH}_2-$  or  $-\text{CFH}-$  in the main chain and has nothing to do with the terminal groups. That is, the perfluoropolymer of Curtin et al will always have end groups “free of C-H bonds,” unless it is a quaternary amine cation associated with the  $\text{SO}_3$  group (which Curtin et al explain is one of the exceptions to “free of C-H bond”).

If there are unfluorinated sites such as VDF unit in the polymer, the polymer indicates bands at  $2800\text{--}3000\text{ cm}^{-1}$ . The polymer with  $-\text{SO}_3\text{NR}_4$  also indicates bands at  $2800\text{--}3000\text{ cm}^{-1}$ . However, there is no such band in the IR-profile shown in Graph 1 above because the polymer has neither unfluorinated sites nor quaternary amine cation.

Thus, “free of C-H bonds” does not mean “free of unstable carboxyl end groups.”

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are



DECLARATION UNDER 37 C.F.R. § 1.132  
U.S. Application No.: 10/571,317

Attorney Docket No.: Q93199

punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: February 9, 2010.

Tadashi Ino  
Tadashi Ino